ON THE CATALYTIC ACTION OF JAPANESE ACID EARTH. IX. THE PROMOTION AND POISONING OF THE CATALYTIC ACTION.*

By Koshiro ISHIMURA.

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The behaviours of the chief constituents of Japanese acid earth in its catalytic action on naphthalene have been elucidated,[1] but the rôle played by water contained in the earth has been left untouched. It has now been found that water exerts a distinct promoting action in that catalysis. Several neutral substances containing oxygen in their molecules such as methyl and ethyl alcohols, acetone, and ether have also proved to be promotors similar to water, and those which contain nitrogen such as ammonia, methylamine, acetonitrile, and amyl nitrite behave as strong poisons, while acidic substances such as hydrogen chloride and acetic acid are quite weak poisons. Chloroform, carbon tetrachloride, chlorobenzene and many hydrocarbons have been found indifferent to the catalytic action.

The acid earth used almost exclusively in the present experiment is that which has been designated earth F in the previous papers, and its catalytic activity on naphthalene measured by the yield of the resinous matter under the " standard condition " is, as stated in the previous paper,[2] 2.23. This value was taken as the standard for the comparison of the activity throughout the present experiment, unless specially mentioned.

The Action of Water. With the rise in the drying temperature of the acid earth its catalytic activity decreases rapidly, the liberation of water from the earth being observed simultaneously as shown in Fig. 1 and Table 1.[3]

The experiments were carried out under the " standard condition " in the determinations of the activities except that the samples were dried at respective temperatures for one hour. The amounts of water set free were estimated after the constant weights were obtained at respective temperatures.

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* An epitomized translation of the original published in Vol. 29 of the Reports of the Tokyo Imperial Industrial Research Laboratory.

(1) Inoue and Ishimura, This Bulletin, **9** (1934), 431.

(2) Loc. cit.

(3) 97 Per cent. or more of the ignition loss is due to the liberation of water. Kobayashi, Yamamoto, and Bito, *J. Soc. Chem. Ind. Japan*, **32** (1929), 998.

Table 1.

Temp. of drying	To 50°	50–120°	120–200°	200–250°	250–300°	300–500°	Above 500°
Water set free (%)	3.33	3.73	0.76	0.62	0.27	1.03	3.97

The decrease in the catalytic activity of the earth shown in Fig. 1 may not be ascribed only to the effect of the heat treatment, since water may play some rôle in the catalysis. In order to ascertain whether water influences the catalysis or not, it is necessary to procure the specimens of the earth containing the different amount of water with the same heat treatment. The earth dried at 300° adsorbs water vapour rapidly when brought into contact with the saturated vapour at room temperature and when the moist earth thus obtained is dried again at 120° it liberates almost all the water adsorbed, but a small fraction of it is always held by the earth even after the drying is continued for about 10 hours until the weight of the earth becomes constant. The water retained at the end of this treatment will be hereafter called, for convenience' sake, "retained water".

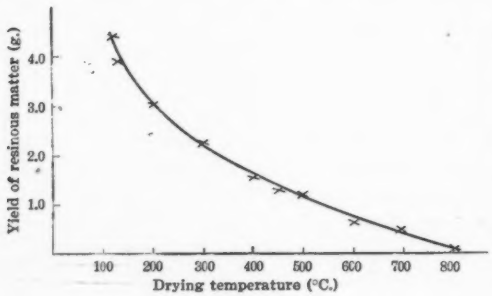

Fig. 1.

The amount of the retained water is a function of the total amount adsorbed as shown in Fig. 2. Thus several samples of the earth with different water content after the same heat treatment are obtainable, and it will be safely stated that if their catalytic activities under the same condition differ from one another it may be entirely ascribed to the difference of the amount of water contained in them.

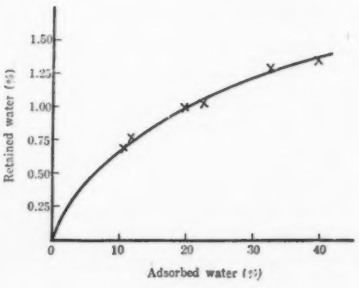

Fig. 2.

The relation between the amount of the retained water and the cataly-

tic activity is shown in Table 2, which indicates that the larger the former is the greater the latter, in other words, the retained water exerts a decided promoting action in the catalysis.

Table 2.

Time of adsorption (days)	0	10 (hrs.)	1	7	13	21	33
Water adsorbed (%)	0	5.16	9.42	22.8	26.3	32.9	38.9
Water retained (%)	0	0.66	1.06	1.35	1.47	1.69	1.87
Yield of resinous matter (g.)	2.23	2.49	2.75	3.08	3.08	3.42	3.59
Increase in resinous matter (g.)	—	0.26	0.52	0.85	0.85	1.19	1.36

Though about 10 hours are required to get the constant weight when the moist earth is dried at any temperature, about 98 per cent. or more of the total water to be liberated is set free within 2 hours. The amount of the retained water after 5 hours' drying are plotted in Fig. 2 and those after 2 hours' drying are tabulated in Table 2, and in all the experiments described below the duration of drying was fixed at 2 hours.

The catalytic activities of the earth treated at 500° and 800° are also promoted by the retained water as shown in Table 3.

Table 3.

Temperature of pre-treatment	500°				800°	
Time of adsorption (days)	0	2	2(4)	16	0	18
Water adsorbed (%)	0	9.01	15.1	22.2	0	9.0
Water retained (%)	0	0.26	0.39	0.55	0	0.2
Yield of resinous matter (g.)	1.20	1.66	1.95	2.06	0.11	0.17
Increase in resinous matter (g.)	—	0.46	0.75	0.86	—	0.06

(4) Owing to the differences of temperature and vapour pressure, the different values of adsorbed water are obtained after equal time of adsorption.

If a represents the yield of the resinous matter produced by the earth and b the increase in the yield caused by the retained water, then a quantity $(b/a)\times 100$ may be designated "degree of promotion". The degrees of promotion calculated from the data given in Table 2 and 3 are plotted against the amounts of the retained water expressed in millimols as shown in Fig. 3.

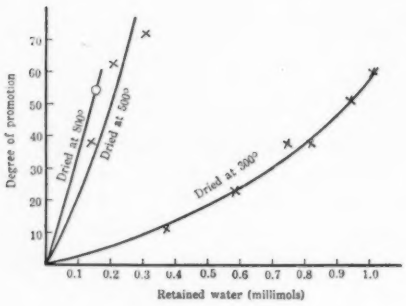

Fig. 3.

The water simply adsorbed by the dry earth as well as that added in the reaction tube in liquid state also promotes the reaction, but their promotive powers fall far behind that of the retained water as will be seen in Table 4.

Table 4.

Kind of water	Retained	Adsorbed	Added	Retained	Added
Amount of water (%)	1.70	1.99	1.93	1.87	5.14
Yield of resinous matter (g.)	3.38	2.31	2.31	3.59	2.87
Increase in resinous matter (g.)	1.15	0.08	0.08	1.36	0.45

Now, when the desorption of water from the moist earth takes place, the molecules of water stored in large capillaries in liquid state or those localized on the upper layers of the adsorbed film would be liberated first, and those held directly on the bare surface would remain to the very last, representing the retained water above designated. The data given in Table 4 seem to show that it is these water molecules adsorbed directly—therefore the most firmly held—on the surface that promote the catalysis but not those more loosely adsorbed or those simply present in the reaction system.

If, in the course of the adsorption, the monomolecular film of water is formed on the whole surface before there occurs the formation of any polymolecular film, the amount of the retained water would represent the total amount of the water adsorbed in the early stage of the adsorption and the former would become independent of the latter if once the whole surface is covered. As a matter of fact, however, this is not the case. As will

be suggested in next communication, the amount of water needed to cover the whole surface of the dry earth represents about 2.5 per cent. of the weight of the earth on the assumption of a packed monomolecular layer. Fig. 2 and Table 2 show that the proportionality between the amount of retained water and the total amount adsorbed extends far above this limiting value. It would appear therefore that the formation of the polymolecular layers as well as capillary condensation commences long before the whole surface is covered with a monomolecular layer. Hoover and Rideal[5] came to the same conclusion from a different view point in the case of the adsorption of ethyl alcohol on thoria.

The Actions of Oxygen-containing Neutral Substances other than Water. Methyl and ethyl alcohols, acetone, and ether were examined and all of them were found to promote the reaction to a marked degree. All materials were cautiously purified by appropriate methods. The adsorption of vapours was carried out in a desiccator at saturated vapour pressures and the retained amounts were determined by the same method as the above-mentioned. As in the case of water, the amount of each retained substance was found to be a function of the total amount adsorbed. The plots of degrees of promotion against the retained amounts expressed in millimols of the respective substances are shown in Fig. 4.

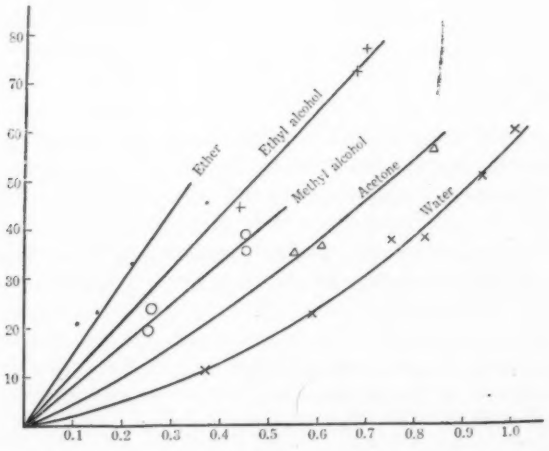

Fig. 4.

(5) *J. Am. Chem. Soc.*, **49** (1927), 122.

The order of magnitudes of the degrees of promotion corresponding to the same millimols of the retained substances can be easily given from Fig. 4 as follows:—

Ether > ethyl alcohol > methyl alcohol > acetone > water.

Gurwich[6] has studied the heats of adsorption of various organic liquids when brought into contact with Fuller's earth[7] as well as the dispersive powers which were measured by the percentage of Fuller's earth remaining in suspension in those liquids after shaken up with them. The results of his determinations[8] are given in the second and third columns of Table 5.

Table 5.

Substance	Heat of adsorption	Dispersive power (%)	Dielectric const. (18°)	Surface tension (20°)[9]	Solubility of naphthalene (0°)[10]
Ether	10.7	0.90	4.36	16.49	large
Ethyl alcohol	17.2	—	20.8	22.03	0.0209
Methyl alcohol	21.8	1.60	31.5	23.02	0.0087
Acetone	27.3	1.72	21.5 (20°)	23.35 (16.8°)	—
Water	30.2	2.85	81.1	70.60	0.0000

The order of the magnitudes of both the heats of adsorption and dispersive powers determined by Gurwich is exactly reverse to the order of the degrees of promotion observed by the present author. The regularity of this relation is very striking. It is also noticed that the solubility of naphthalene, the dielectric constant, and the surface tension of the liquids go either parallel or reverse to the degree of promotion as shown in Table 5.

(6) *J. Russ. Phys. Chem. Soc.*, **47** (1915), 805.

(7) Japanese acid earth is in many respects similar to Fuller's earth, and it is generally accepted that the former is a species of the latter.

(8) Cited from Langmuir's paper. *J. Am. Chem. Soc.*, **39** (1917), 1898.

(9) This column represents the surface tensions expressed in dynes per cm. in the atmospheres of the saturated vapours of the respective substances.

(10) The solubility of naphthalene is expressed in mols per mol of the respective solvent. The solubility in acetone is not found in literature, so far as the author knows.

As will be fully discussed in next communication, the catalytic action of Japanese acid earth on naphthalene may be considered to be brought about by the three component catalyst consisting of Al_2O_3, SiO_2, and water, and when molecules of naphthalene are adsorbed on the catalytically active centres formed by these three components they are activated so as to produce β,β'-dinaphthyl. When the earth is heated to 300° the liberation of water from some of these active centres takes place rendering them incapable of participating in the catalysis. They will, however, recover their ability if water molecules are again put in their original positions. This recovery of catalytic activity is accomplished by the retained water when the earth is brought into contact with water vapour, giving rise to the observed promotion of the activity. Moreover, the molecules of water to form the active centres are replaceable by those of neutral substances such as alcohols, acetone, and ether, and the similar promoting action is effected by them.

The degree of promotion depends therefore upon both the number of the active centres thus recovered and the number of molecules of naphthalene to be activated on each of these new centres, in other words, upon the number and the intensity or the mean life of new active centres.

Table 5 shows that, the greater is the degree of promotion the smaller the heat of adsorption and the dispersive power and the larger the solubility of naphthalene. The heats of adsorption and the dispersive powers would be considered as measures of the molecular affinities between these various liquids and the acid earth, while the solubilities of naphthalene as measures of the molecular affinities between these liquids and naphthalene. The author is inclined to believe that the former is connected with the number of the active centres to be recovered and the latter with the intensity or the mean life of these centres to activate the molecules of naphthalene adsorbed on them, that is, the larger the molecular affinity between the vapour and the acid earth the more difficult becomes the formation of the active centres, and the larger the molecular affinity between the vapour and naphthalene the stronger is the intensity or the longer is the mean life of the active centres. Dielectric constant and surface tension are in close connection with the molecular structure and the orientation of molecules on the surface of liquids respectively, and it may be anticipated that these quantities would bear some relationship with the catalytic activity.

It is tempting to go on studying how Al_2O_3, SiO_2, and oxygen-containing neutral substances must be configurated in order to form the active centres and how molecules of naphthalene must be oriented on them in order to be activated, and further study on these lines is expected to be carried out in near future.

The Action of Hydrogen Chloride, Acetic Acid, and Ethyl Acetate. The acidic substances such as hydrogen chloride and acetic acid (and most probably hydrogen sulphide, too) are quite weak poisons to the catalytic action. Their total amounts adsorbed are fairly small compared with the neutral substances. Table 6 shows the results of experiments on these substances as well as ethyl acetate.

Table 6.

Substance	Hydrogen chloride		Acetic acid	Ethyl acetate
Amount adsorbed (%)	2.23	—	5.96	20.03
Amount retained (%)	0.33	1.21 (added)	5.58	4.20
Amount retained (millimol)	0.09	0.33	0.93	0.48
Yield of resinous matter (g.)	2.25	2.01	2.01	2.44
Decrease in yield (g.)	0	0.22	0.22	0.21 (increase)
Decrease in yield (%)	0	10	10	10 (increase)

Ethyl acetate is a neutral substance and moreover values of both the heat of adsorption and dispersive power determined by Gurwich lie between those of methyl alcohol and ether; therefore it seems very reasonable that it would make a promotor as strong as the alcohol at least. The fact is, however, that it proved to be a very weak promotor as will be seen from Table 6. This may be explained by the experiment by Dr. Inoue[11] that ethyl acetate is decomposed by the catalytic action of Japanese acid earth giving acetic acid, the poison to the reaction.

The Actions of Nitrogen-containing Substances. Ammonia and methylamine are the most strong poisons, while acetonitrile and amyl nitrite are milder in their poisoning actions as shown in Table 7.

(11) *J. Soc. Chem. Ind. Japan*, **28** (1925), 598.

Table 7.

Substance	Ammonia	Methylamnie	Acetonitrile	Amyl nitrite
Amount adsorbed (%)	5.49	5.66	27.06	61.05
Amount retained (%)	0.84	4.45	3.08	16.02
Amount retained (millimol)	0.49	1.43	0.75	1.36
Yield of resinous matter (g.)	0	0	0.28	0.23
Decrease in yield (g.)	2.23	2.23	1.95	2.00
Decrease in yield (%)	100	100	88	90

The Actions of Hydrocarbons, Chlorine-containing Neutral Substances, and Thiophene. It should be noted that the retained amounts of these substances are in general very small unless the adsorbed substance is decomposed by the catalytic action of the earth at room temperature as in the case of alicyclic unsaturated hydrocarbons. Benzene, toluene, cyclohexane, cyclohexene, and methylcyclohexenes were examined and all of them were found to be indifferent to the reaction. It does not matter whether these substances were retained, adsorbed or added or entirely absent. The yield of the resinous matter was always equal within the experimental error. Chlorobenzene behaves similarly. Chloroform and carbon tetrachloride are also indifferent as long as their amounts are small, but if they are added in relatively large quantities the yield of the resinous matter is decreased to some extent, the evolution of hydrogen chloride being observed simultaneously. It appears therefore that they are non-poisonous in themselves, and their apparent poisoning action is to be ascribed to hydrogen chloride produced by the catalytic action of the earth.

The experiments hitherto carried out with thiophene are not sufficient to draw any decided conclusion thereby. It may be only mentioned here that when thiophene is added in fairly large quantity the slight poisoning effect is observed, accompanied by the evolution of hydrogen sulphide.

Summary.

(1) The catalytic action of Japanese acid earth on naphthalene is greatly promoted when it contains the "retained water", designated temporarily by the present author.

(2) The molecules of the "retained water" may be replaced by those of several other neutral substances containing oxygen in their molecules, the catalytic activity of the earth being thereby raised to a greater or smaller extent according to the nature of the substance.

(3) The term "degree of promotion" has been introduced, and the relation between the degree of promotion and molecular affinity has been discussed.

(4) The nitrogen-containing substances such as ammonia, methylamine, acetonitrile, and amyl nitrite have been found to be strong poisons to the catalysis, while the acidic substances such as hydrogen chloride and acetic acid have proved to be quite weak poisons.

(5) Chloroform, carbon tetrachloride, chlorobenzene, and many hydrocarbons have been found indifferent to the catalytic action.

The author wishes to express his cordial thanks to Dr. Inoue for his interest and encouragement taken in this study.

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THE BENZYL ETHERS OF POLYSACCHARIDES. I. THE BENZYL ETHERS OF STARCHES OF VARIOUS ORIGINS.

By Tei-ichi ASAHINA and Gengo NARA.

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The preparation of benzyl ethers of mono- and poly-saccharides was first reported by Gomberg and Buchler.[1] Of those, cellulose benzyl ethers have been continually studied and proved to give products of good quality. At present they are manufactured to reply the demand as lacquer constituents. The benzyl ethers of other polysaccharides, however, have scantily been investigated.[2]

(1) M. Gomberg and C. C. Buchler, *J. Am. Chem. Soc.*, **43** (1921), 1904.

(2) Brit. P., 149320 (1921); Lilienfeld, D.R.P., 360415 (1922); F.P., 534778 (1921); I.G. Farbenindustrie, Austrian P., 12780 (1932).

Gomberg and Buchler reported that, under their experimental conditions, the benzyl ether obtained from potato starch was not identical with that from corn starch in respect of the composition. From potato starch they obtained monobenzyl ether of the composition corresponding to $C_{12}H_{19}O_{10}\cdot C_7H_7$, while from corn starch, dibenzyl ether of the composition corresponding to $C_{12}H_{18}O_{10}\cdot 2C_7H_7$. They do not seem to have made much further studies on these two different ethers: their melting points and solubilities in some organic solvents did not differ much from each other. There is, however, no explanation by those authors on the difference in behaviours of the different kinds of starches. It is interesting that the starches from different origins gave products of different degrees of benzylation under the same conditions. From this point of view we have undertaken the benzylation of starches from various plants, as they are easily accessible in our country.

For the present, the potato starch, corn starch, wheat starch, "Kuzuko" (starch powder prepared from the root of *Pueraria triloba*, MAKINO) and "Warabi-ko" (starch prepared from the root of *Pteridium aquilinum*, KUHN, var. *japonicum*, NAKAI) have been brought under investigation.

Alien from the results reported by Gomberg and Buchler, these starches gave exclusively the dibenzyl ethers of the composition corresponding to $C_{12}H_{18}O_{10}\cdot 2C_7H_7$ under our experimental conditions which did not differ much from those mentioned by them. At first our results of elementary analyses of the products corresponded neither to mono- nor to di-benzyl ether of starch, but on strictly desiccating them, the figures obtained were quite identical with those calculated for dibenzyl ether, well within the limit of experimental errors. The melting points of the products were either discordant from those observed by Gomberg and Buchler. Though the melting points of such amorphous substances cannot be generally expected to be very sharp, the discordance was very much remarkable. Of all the products the melting points were found to lie between 165° and 175°. Furthermore we made polarimetrical measurements of the benzyl ethers from various starches, which showed nearly the same rotatory power.

From our experiments, we cannot definitely gainsay the results obtained by Gomberg and Buchler, but there can be some doubtful points there.

Whether our products which we consider to be dibenzyl ethers from the figures of elementary analyses only, are really so, or mixtures of benzyl ethers of different degrees of benzylation, cannot be determined from the results so far obtained. The matter needs further study, and shall be treated in following reports.

Experimental.

(1) **Preparation of Benzyl Starches.** The starch was dried in an air-oven at 80–90° for some hours. To 1 mol (8 g.) of the dried starch, 4.5 mols (9 g.) of 9% caustic soda and 3.5 mols (22 g.) of benzyl chloride were added. They were well blended in a wide-necked conical flask by shaking vigorously; thus a thick, translucent, homogeneously dispersed liquid was obtained which was heated under occasional shaking in a water bath kept at 80–85° about four hours. In the course of one hour and a half a gummy mass separated and after that no remarkable change was observed. The mode of reaction was nearly the same for all the species of starch used.

(2) **Purification of the Products.** The solution was decanted from the gummy mass and the latter was subjected to steam distillation to remove occluded benzyl chloride and some impurities produced during the reaction. The mass did not come to pieces and the trace of the impurities could not be removed in this way. The steam distillation was stopped; the mass in the flask was drained and pulverised in the mortar with the addition of a small quantity of ether to dissolve the impurities. After repeated washing with fresh ether, the powder was dried in the air-oven at 80–90°. The yield is shown in Table 1, that calculated for mono- and di-benzyl ethers being 10.2 g. and 12.4 g. respectively.

Table 1.

Origin of starch	Potato	Corn	Sweet potato	Wheat	"Kuzu"	"Warabi"
Yield of benzyl ether	11.7 g.	11.4 g.	11.2 g.	11.0 g.	11.3 g.	11.2 g.

The crude products were all more or less discoloured to slightly yellow; the discoloration of that from "Warabi" starch was the most remarkable. The product was dissolved in a small quantity of glacial acetic acid and filtered from minute fragments of insoluble matters through a hot funnel. To the filtrate, pure ether sufficient to precipitate the product was added. The supernatant ethereal solution was decanted and the separated white powder was repeatedly washed with fresh ether to remove the trace of acetic acid. The repetition of the procedure seems to give products of no further purity when we judge from the data of elementary analyses and the inspection of the melting points. The product from "Warabi" starch was three times precipitated in this way.

(3) **Elementary Analyses.** The elementary analysis is the only simplest way to determine the degree of benzylation.[3] The product was dried in the air-oven at 80–90° until the weight was constant and it was kept in the desiccator. Before analysis, the sample was dried in Abderhalden's desiccating apparatus in vacuo at 110°; the figures (Table 2) given in the columns designated by I were calculated, with the correction of moisture content, from the values obtained with the samples which were not dried in Abderhalden's apparatus. The mean value of the carbon content lies between 60.43 and 60.78% and that of hydrogen between 6.35 and 6.53% and they are well coincident with those calculated for $C_{12}H_{18}O_{10}\cdot 2C_7H_7$ (C, 61.92; H, 6.35%), and not for $C_{12}H_{19}O_{10}\cdot C_7H_7$ (C, 55.07; H, 6.28).

Table 2. Analyses of Benzyl Ethers from

Potato Starch

	H (%)	C (%)	Ash (%)
I	6.44	60.80	—
	6.59	60.79	—
II	6.37	61.48	0.3
	6.51	60.22	—
	6.66	61.01	0.4
	6.60	60.65	—
	6.53	60.52	0.3
Mean	6.53	60.78	0.3

Corn Starch

	H (%)	C (%)	Ash (%)
I	6.49	61.05	—
	6.55	60.88	—
	6.32	60.70	—
II	6.54	61.18	—
	6.26	60.69	—
	6.34	60.15	0.4
Mean	6.42	60.78	0.4

Sweet Potato Starch

	H (%)	C (%)	Ash (%)
I	6.26	59.79	—
	6.45	60.74	—
	6.29	60.64	—
	6.25	60.31	—
II	6.44	60.64	0.4
	6.40	60.37	0.4
	6.37	60.54	—
Mean	6.35	60.43	0.4

Wheat Starch

	H (%)	C (%)	Ash (%)
I	6.57	61.41	—
	6.74	60.99	—
	6.45	60.52	—
	6.41	60.03	—
	6.31	59.99	—
II	6.53	61.28	—
	6.46	60.45	—
	6.46	60.14	0.3
Mean	6.49	60.60	0.3

(3) The method proposed by Meunier and Gonfard seems rather tedious. *Compt. rend.*, **134** (1932), 1839.

Table 2. (*Concluded*)

"Kuzu" Starch

	H (%)	C (%)	Ash (%)
II	6.37	60.93	—
	6.69	60.76	0.3
	6.31	60.41	0.4
Mean	6.46	60.70	0.4

"Warabi" Starch

	H (%)	C (%)	Ash (%)
II	6.46	60.69	—
	6.69	60.39	—
	6.14	60.57	0.5
Mean	6.43	60.55	0.5

(4) **Melting Points and Specific Rotations.** These are shown in Table 3. In the measurement of optical rotations, ethylene chlorohydrin of b.p. 127.5–128.5° was used as the solvent, the concentration being about 3 per cent. and the temperature about 30° (Table 3).

Table 3.

Origin of starch	Melting point (°C.)	Rotation		
		Conc. (g./dl.)	Temp. (°C.)	$[\alpha]_D$
Potato	170–172	2.986	30.6	+118.3
Corn	170–172	3.025	30.7	+120.1
Sweet potato	169–172	3.013	30.8	+117.1
Wheat	169–171	3.015	31.1	+120.8
"Kuzu"	165–169	3.003	31.2	+118.5
"Warabi"	170–172	3.000	31.1	+118.1

As the light-source for the polarimetric measurement, we used a sodium-flame produced by a glass-work burner: a pinch of asbestos wetted with a strong solution of sodium carbonate or caustic soda and dried in the flame of a Bunsen burner, is fastend with copper wire and put into the flame near the jet of the glass blowing burner. Instead of air blast, a moderate stream of oxygen is supplied from the bomb. The brightness of the light source is comparable with that of a small electric sodium lamp.

Quite recently A. I. Schattenstein[4] reported an analogous idea on the use of oxygen-coal-gas flame as a monochromatic light source of D-line. Sodium chloride and bromide which he used cannot be recommended, for, although the intensity of the flame is great, much smoky sublimate is produced and this makes the air of the laboratory very dirty.

(4) A. I. Schattenstein, *Z. anal. Chem.*, **98** (1934), 235.

STUDIES ON AMINO-ACIDS AND RELATED COMPOUNDS. PART VIII. ELECTROLYTIC OXIDATION OF HISTAMINE AND HISTIDINE.

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In a previous communication,[1] it was stated that imidazolyl-propionic acid was readily oxidized at the anode and the rupture of imidazol nucleus resulted. In the present paper studies on histamine and histidine are reported and the mechanism of oxidation of these three kindred compounds are discussed. They have the same heterocyclic nucleus, and differ only in the functional grouping attached to the side-chain.

Among various studies on histidine, subjects allied to the present work are treated in the following communications.

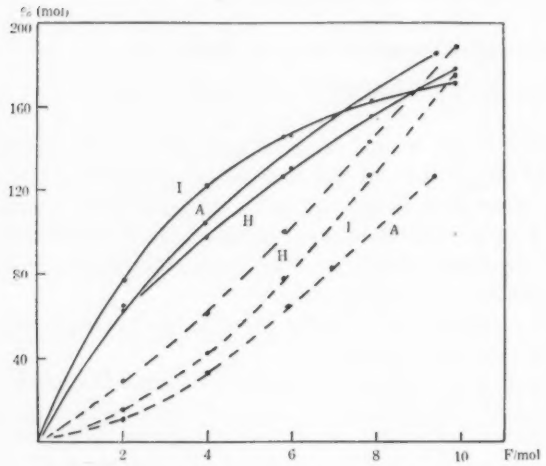
In 1907 Knoop[2] reported on the oxidation reactions of histidine and its derivatives and in his study he established the constitution of this amino-acid. He oxidized imidazolyl-lactic acid $C_3H_3N_2 \cdot CH_2 \cdot CH(OH) \cdot COOH$ (I) with concentrated nitric acid and obtained imidazolyl-glyoxylic acid $C_3H_3N_2 \cdot CO \cdot COOH$ (II) which was further oxidized to imidazol-carboxylic acid $C_3H_3N_2 \cdot COOH$ (III) by the action of hydrogen peroxide in the presence of acetic acid. On the other hand, oxidation of (I) with barium permanganate yielded imidazolyl-acetic acid $C_3H_3N_2 \cdot CH_2 \cdot COOH$ (IV). He also stated that histidine $C_3H_3N_2 \cdot CH_2 \cdot CH(NH_2) \cdot COOH$ itself yielded the same products (II and III) when oxidized with nitric acid, but it was not so readily attacked. In 1909 Langheld[3] found that imidazolyl-acetaldehyde $C_3H_3N_2 \cdot CH_2 \cdot CHO$ was a reaction product when histidine hydrochloride was oxidized with sodium hypochlorite. In 1916 Dakin[4] obtained cyanomethyl-imidazol $C_3H_3N_2 \cdot CH_2 \cdot CN$ by oxidizing histidine with toluene-*p*-sulphochloramide.

In none of these papers the rupture of imidazol nucleus is mentioned and no investigation is found on the electrolytic oxidation of this amino-acid.

The authors have first examined the oxidizability of histamine by the method already described[5] (Fig. 1), and compared it with those compounds

(1) Y. Takayama, this Bulletin, **8** (1933), 189.
(2) Fr. Knoop, *Beitr. chem. Physiol. Pathol.*, **10** (1907), 111.
(3) K. Langheld, *Ber.*, **42** (1909), 2373.
(4) H. D. Dakin, *Biochem. J.*, **10** (1916), 319.
(5) Y. Takayama, this Bulletin, **8** (1933), 213.

previously dealt with. The curves representing the course of formation of carbon dioxide and ammonia from this amine by electrolysis are of the same type as those of imidazolyl-propionic acid and histidine. From this fact it can be easily expected that the courses of oxidation of these allied compounds do not show marked diversity. But they indicated obvious difference in one point, namely, in the colour of their electrolysates. The electrolysates of imidazolyl - propionic acid and histamine assumed yellowish tint as the electrolysis proceeded and never turned to black until the end while that of histidine changed to black and considerable amount of a melanin - like substance separated.



NH_3-curves (——), CO_2-curves (– – –)
I = Imidazolyl-propionic acid.
H = Histidine.
A = Histamine.

Fig. 1.

Separation of Oxidation Products of Histamine. Histamine in dilute sulphuric acid solution was electrolyzed with a lead peroxide anode and a lead cathode, conditions being similar to those in the case of imidazolyl-propionic acid, current quantity applied 6 faradays per mol, and the temperature 30°C. The electrolysate was treated with phosphotungstic acid and the precipitate (A) formed was separated from the filtrate (B).

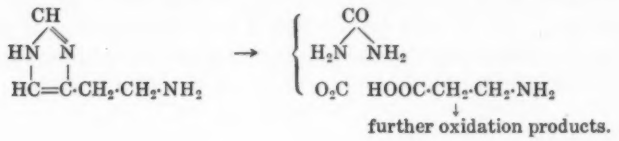
Precipitate (A). Ammonia and unchanged histamine were isolated as volatile and non-volatile bases respectively.

Filtrate (B). Urea was estimated in this part by urease method, the amount corresponding to 7.7%.* β-Alanine (8.5%) was also obtained from the concentrated solution on treatment with alcohol and ether and it was confirmed as such by converting it into α-naphthylisocyanate compound.

* Small amounts of urea (1.3%), and ammonia (1.0%) were also found in (A), thus total quantity of urea amounting to 9.3% and that of β-alanine 12.0%.

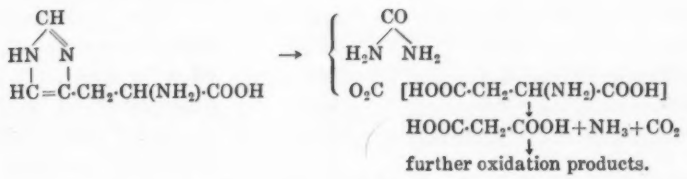
As β-alanine is said to be unstable to alkali,[6] its amount can be presumed by the estimation of ammonia formed on treatment with caustic alkali. The amount of β-alanine thus found was 11.1%, under the assumption that no other substance yielding ammonia by this treatment was contained.

The Mechanism of the Reaction. The products obtained from histamine in the above oxidation comprise urea (9.0%), β-alanine (8.5%; 12.0%), ammonia, and carbon dioxide. Considering the isolation of these substances as the basis, the course of the oxidation can be explained as follows:



Separation of Oxidation Products of Histidine. Histidine was electrolyzed just in the same manner as above. A melanin-like substance formed during electrolysis was separated after long standing and its nitrogen content was found 13.64%. The electrolysate was treated with phosphotungstic acid as usual. Ammonia and urea (11.1%) together with unchanged histidine were isolated.

Urea was obtained in each of these three cases and it would result from the rupture of imidazol nucleus, and in two previous cases succinic acid semi-aldehyde together with succinic acid and β-alanine were found respectively as the other fragments. In the case of histidine, aspartic acid was expected by analogy to be the first oxidation product, but, in point of fact, it could not be isolated. On the other hand, a small quantity of malonic acid (about 3%)[7] was found, which may be assumed to be produced by the further oxidation of aspartic acid. The oxidation of histidine may be represented as follows:



(6) E. Abderhalden and A. Fodor, *Z. physiol. Chem.*, **85** (1913), 112.

(7) Malonic acid is also unstable to oxidation, hence, its poor yield. F. Lieben and E. Molnar, *Monatsh.*, **53** (1929), 7.

The electrolytic oxidation of these kindred compounds, namely, imidazolyl-propionic acid (I), histamine (II) and histidine (III) proceeded through a similar course, imidazol nucleus being attacked and yielding urea. Besides urea, (I) gave succinic acid semi-aldehyde and succinic acid, and (II) gave β-alanine, the same being the case with histidine (III). The latter gave, besides urea, aspartic acid, and this, being too unstable to remain unattacked, was completely oxidized, a part of the product remaining in its intermediate stage as malonic acid.

The formation of a melanin-like substance was restricted to one case, namely, histidine, and it may be concluded that the presence of the cyclic ring together with amino-group in the α-position to the carboxylic group is necessary for its formation.

Experimental Part.

Electrolytic Oxidation of Histamine. Histamine (synthesized)* which was used gave the following analytical result:

Found: N, 37.33. Calc. for $C_5H_9N_3$: N, 37.83%.

The course of formation of carbon dioxide and ammonia during electrolysis was determined after every definite consumption of electricity[8] (Table 1).

Histamine (4.45g., about 40 milli-mols) was dissolved in 100 c.c. of 2N sulphuric acid and the solution was electrolyzed. Cell: without diaphragm; Electrodes: lead—lead peroxide (3.8 cm. × 5.5 cm.), distance 1.5 cm.; C.D.: 2 amp./dm.^{2}; Electric quantity applied 6 F./mol.

Table 1.

Current quantity (F./mol)	CO_2/Histamine (mol %)	NH_3/Histamine (mol %)
1.97	9.7	60.4
3.94	34.3	102.7
5.90	67.1	130.2
6.93	82.3	154.8
9.42	126.3	182.7

The electrolysate was thoroughly extracted with ether. A small quantity of oil insoluble in water was obtained from the extract, but its quantity was too minute for further investigation.

* The sample of histamine was kindly offered by Mr. S. Numano, to whom the authors express their thanks.

(8) Cf. Y. Takayama, this Bulletin, 8 (1933), 213.

The residue of the extraction was diluted with 5% sulphuric acid and 20% phosphotungstic acid was added to it.

Precipitate (A). It was decomposed with barium hydroxide, the solution was distilled under reduced pressure at 60°C., and the distillate was received in hydrochloric acid. The hydrochloride of the base was not hygroscopic. It was extracted with cold absolute alcohol. Bases obtained from the extract and the residue were found to be ammonia by the analysis of their platinic double chlorides.

Found for the substance from the extract: Pt, 43.16. Found for the substance from the residue: Pt, 43.72. Calc. for $(NH_4)_2PtCl_6$: Pt, 43.93%.

After removal of barium exactly, the part containing non-volatile base was concentrated under reduced pressure, but it was impossible to bring it into crystallization. The concentrated bulk was treated with picric acid and the base precipitated as picrate. It amounted to 5% and melted at 227°C. after recrystallization from water, coinciding with histamine dipicrate. No other base was obtained from the filtrate of the picrate.

Found: N, 22.28. Calc. for $C_5H_9N_3 \cdot 2C_6H_3O_7N_3$: N, 22.15%.

Estimation of urea (urease method):

Solution taken: 1/20 part.* $NH_3 = 3.58$ c.c. of N/70 $H_2SO_4 = 0.0512$ milli-mol.

Calculating into total volume, $NH_3 = 1.02$ milli-mols, hence, urea = 0.510 milli-mol (1.3%).

Estimation of β-alanine (NH_3** formed on heating at 100°C. for ten minutes with excess of caustic soda):

Solution taken: 1/20 part. $NH_3 = 1.46$ c.c. of N/70 $H_2SO_4 = 0.0209$ milli-mol.

Calculating into total volume, $NH_3 = 0.42$ milli-mol (1.0%).

Filtrate (B). The solution, after removing barium with carbon dioxide and sulphuric acid, was concentrated to 100 c.c. by evaporation under reduced pressure. The amount of urea and β-alanine was determined.

Estimation of urea (urease method):

Solution taken: 1.00 c.c. out of 100 c.c. $NH_3 = 4.28$ c.c. of N/70 $H_2SO = 0.0612$ milli-mol.

Calculating into total volume, $NH_3 = 6.12$ milli-mols, hence, urea = 3.06 milli-mols (7.7%).

Estimation of β-alanine:

Solution taken: 1.00 c.c. out of 100 c.c. $NH_3 = 3.07$ c.c. of N/70 $H_2SO_4 = 0.0439$ milli-mol.

Calculating into total volume, $NH_3 = 4.39$ milli-mols (11.0%).

The remaining part of the solution was concentrated to a syrup, after decolourization with animal charcoal. The syrup was dissolved in dilute alcohol and an excess of ether was added to it until faint turbidity appeared.

* It was confirmed by the same aeration method that no trace of free ammonia was present in the solution.

** It was ascertained that histamine itself does not yield an appreciable amount of ammonia by this treatment.

The turbidity of the solution soon disappeared, an oil depositing at the bottom, which changed to crystals after long standing. The yield amounted to 0.30 g. (8.5%). The crystalline substance was dissolved in a small bulk of water and recrystallized by adding alcohol. It melted at 198–200°C. coinciding with β-alanine.[9]

Found: N, 16.03. Calc. for $C_3H_7O_2N$: N, 15.73%.

β-Alanine was dissolved in twice its equivalent of N NaOH, diluted with four times of water, and α-naphthyl-isocyanate (1.2 equivalents) was added to the solution. After one hour, an excess of hydrochloric acid was poured, and α-naphthyl-isocyanate compound of β-alanine precipitated. After recrystallization from alcohol it showed effervescence at 196°C. and melted completely at 226–228°C.[10]

Found: N, 11.01. Calc. for $C_{14}H_{14}O_3N_2$: N, 10.86%.

Electrolytic Oxidation of Histidine. Histidine monohydrochloride (Schuhardt) used gave the following analytical results:

Found: N, 20.04; HCl, 16.94. Calc. for $C_6H_9O_2N_3 \cdot HCl \cdot H_2O$: N, 20.05; HCl, 17.39%.

Histidine monohydrochloride (2.95 g., about 15 milli-mols) was dissolved in 100 c.c. of 2N H_2SO_4. Sufficient water was added to the solution, and it was distilled under reduced pressure to drive off hydrochloric acid. This treatment was repeated several times until the distillate showed no trace of hydrochloric acid. The solution was made up to 100 c.c. and was electrolyzed. The current quantity applied was 8 F./mol.

The electrolysate assumed reddish tint (at 1 F./mol), then gradually changed to black, and a considerable amount of a melanin-like substance deposited on the wall of the vessel and its amount increased in the lapse of time even after the termination of electrolysis. After four months, it was separated, well washed, and analyzed after drying over quick lime. (Found: N, 13.64%.) It is amorphous black powder and readily soluble in alkali.

The electrolysate was diluted with 5% sulphuric acid and treated with phosphotungstic acid.

Precipitate (A). Ammonia was obtained as the volatile base.

Found for the chloroplatinate of the base: Pt, 43.87. Calc. for $(NH_4)_2PtCl_6$: Pt, 43.95%.

After removing barium, the part containing non-volatile base was concentrated to a small bulk. A small quantity of crystals was obtained from

(9) P. Karrer and A. Widmer, *Helvetica Chim. Acta*, **9** (1926), 888.
(10) W. Linneweh, A.W. Keil, and F.A. Hoppe-Seyler, *Z. physiol. Chem.*, **183** (1929), 17.

it, which melted at 258–260°C. with effervescence, after recrystallized from dilute alcohol. It gave positive results in ninhydrine, biuret, and *p*-diazobenzene-sulphonic acid reactions, and its hydrochloride melted at 230–231°C. The base was presumed to be unchanged histidine.

Filtrate (B). After complete separation of barium, the solution was concentrated to 50 c.c. and urea was determined.

Identification of urea (xanthydrol method):

A part of the solution was diluted with glacial acetic acid and the filtered methyl alcoholic solution of xanthydrol (Kahlbaum) was added to it. Urea was precipitated as dixanthyl-urea.

Found: N, 6,74. Calc. for $C_{27}H_{20}O_3N_2$: N, 6.68%.

Estimation of urea (urease method):

Solution taken: 1.00 c.c. out of 50 c.c. NH_3 = 4.67 c.c. of N/70 H_2SO_4 = 0.0667 milli-mol. Calculating into total volume, NH_3 = 3.34 milli-mols, hence, urea = 1.67 milli-mols (11.1%).

Malonic acid: Histidine (25 milli-mols) was electrolyzed as described above. The electrolysate was thoroughly extracted with ether. After expelling ether, brown liquid was obtained from the extract and steam was passed through it to drive off volatile acid. The residue was decolourised and titrated with N/10 NaOH. It required 15.8 c.c., amounting to 0.79 milli-mol as a dibasic acid, which corresponds to 3.0%. The neutralized solution was concentrated and a little excess of N $BaCl_2$ was added to it. A barium salt was precipitated from it by adding 60 per cent. alcohol, which was found to be barium malonate[11] by the analysis after reprecipitation and drying at 100°C.

Found: Ba, 53.99. Calc. for $C_3H_2O_4Ba \cdot H_2O$: Ba, 53.33%.

The barium malonate obtained was dissolved in water and barium was removed as the sulphate. The crystals of the free acid were examined under polarization microscope. It showed oblique extinction, the angle of extinction being 12–13°,[12] and resembled with a pure specimens of malonic acid under the gypsum-plate.

The present work has been carried out in the Chemical Institute, Faculty of Science, Imperial University of Tokyo, and the authors wish to express their sincere thanks to Prof. K. Matsubara for kind inspection of this paper.

(11) C. Coulett, *J. prak. Chem.*, **73** (1906), 76.

(12) P. Groth, "Chem. Krystallographie," III (1910), 230.

REACTIONS BETWEEN ETHYLENE CHLORIDE AND CHLORINE.

By Senzo HAMAI.

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The fact that, when ethylene and chlorine are mixed, a mixture of various chlorinated products in various proportions is formed, has been reported by several investigators.[1] Albert Maier[1] observed that when chlorine and ethylene are mixed in proportion of 2:1 at a temperature between 20° and 30°, the products are found to be 70% 1,1,2-trichlorethane, 15% ethylene chloride, 5% 1,1,2,2-tetrachlorethane, and 10% higher chlorinated products. The difficulties arising from the complex nature of the reaction implicate to the study not only theoretical but also practical importance. Mitsukuri and Kinumaki[2] found that only ethylene chloride is formed when the experiment is carried out at low temperature. Besides, Taylor and Hildebrand[3] published a paper on the solubility of chlorine in ethylene bromide, a compound similar to ethylene chloride, and it was conventionally considered that there was no reaction between chlorine and ethylene chloride; but the evidences so far obtained by the present author definitely show that there are reactions between chlorine and ethylene chloride.

In view of these facts, the study of the reactions of chlorine with ethylene chloride would be very much interesting for clarifying the nature of chlorination of hydrocarbons. Although the work is not yet completed, the purpose of this paper is to point out some of important facts so far found along with some suggestions for the future work.

Materials. Ethylene chloride, from Takeda (b.p. 83.0°), after treated with phosphorus pentoxide and calcium chloride, was subjected to fractional distillation several times, and only the middle portions were used (refractive index 1.44240[4] for H_α-line at 25°).

Chlorine, vaporized from ordinary commercial liquid chlorine in cylinder, was passed through water, concentrated sulphuric acid, and a phosphorus pentoxide tube, condensed by cooling with liquid air or liquid nitrogen, and

(1) A. Maier, German Patent, 522959, Aug. 26, 1926; Stewart and Smith, *J. Am. Chem. Soc.*, **51** (1929), 3091; P. Askenasy and A. Hieler, German Patent, 549341, May 13, 1930.

(2) Mitsukuri and Kinumaki, *J. Chem. Soc. Japan*, **53** (1932), 398.

(3) Taylor and Hildebrand, *J. Am. Chem. Soc.*, **45** (1923), 682.

(4) S. Hamai, This Bulletin, **8** (1933), 297.

vaporized again. This process was repeated three times, the initial and the last portions being rejected each time.

Reaction of Chlorine and Liquid Ethylene Chloride. Chlorine was passed into ethylene chloride in the reaction chamber as shown in Fig. 1. The three ends of the inlet tube A are covered with platinum foils, each with a fine hole, so as to form very minute bubbles of chlorine in ethylene

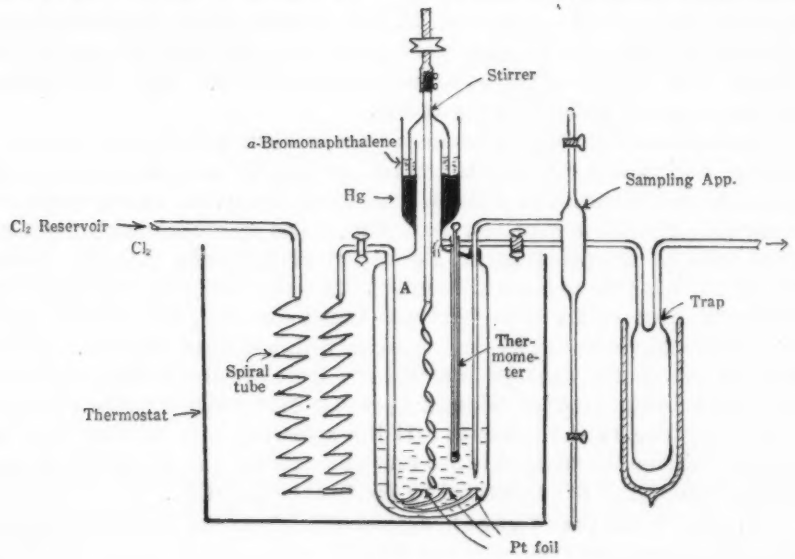

Fig. 1.

chloride. Chlorine was passed for various lengths of time, from 2 to 5 hours, at 50°. The whole reaction vessel was kept in a thermostat, rape-seed oil being used as the thermostat liquid. The rate of flow of chlorine was adjusted to 125–250 c.c. per minute. After a certain time the solution was taken out, washed with sodium hydroxide, dried with calcium chloride, and subjected to fractional distillation. No trace of expected substitution products was obtained. Similar experiments were carried out at 25° and 30°, and chlorine was passed for 2–5 hours with and without radiation by a mercury lamp at both temperatures.

In no case, on treating the mixture as mentioned above, any compound of higher boiling point than ethylene chloride was found; however at the outside of the chamber, in the tube where possibly ethylene chloride vapour

diffused when chlorine was led into the liquid by opening the stopcock, and in one of the traps attached directly to the reaction chamber, the formation of a white crystalline substance was observed after a long while. It was found to be hexachlorethane by its odour somewhat like camphor and m.p. 185°.

In another experiment ethylene chloride was mixed with about one fourth its volume of carbon tetrachloride, and the reaction was carried out under radiation by a mercury lamp.[5] On the following day a crystalline substance was noticed on the wall of the chamber after the solution was taken out, and also the crystals were found, as in the previous case, in the chlorine trap which is attached to the spiral tube of the inlet just outside the thermostat (not shown in the figure).

Correlating with other evidences from previous experiments, this fact possibly means that higher chlorinated derivatives may be formed only where the concentration of chlorine is high and the partial vapour pressure of ethylene chloride is relatively low. This is also concordant with the facts which will be discussed later. Formation of hydrogen chloride is also noticed; this is just as much concordant with the fact that platinum foils used at the ends of the inlet tube was found corroded, for chlorine alone can not possibly corrode platinum, but can with hydrogen chloride. Therefore, the fact that it was unable to find any trace of substituted compounds when the substitution of chlorine for hydrogen in ethylene chloride was tried is probably due to the reasons: (1) the substitution is so slow that on passing chlorine the reaction is not very appreciable, and (2) the substituted amount is too small to be detected by fractional distillation.

In order to see the effect of hydrogen chloride on the reaction, chlorine alone was passed into pure ethylene chloride in one vessel, and in the other, chlorine was passed into ethylene chloride mixed with hydrogen chloride gas, and both were allowed to stand for several hours. Ethylene chloride containing hydrogen chloride decolorized chlorine much faster than that without hydrogen chloride gas. This apparently shows that hydrogen chloride acts as a catalyst in chlorination of ethylene chloride. On fractional distillation, it was found that 1,1,2-trichlorethane was formed (b.p. 113.5°, the refractive index 1.47345[6] for H_α-line at 25°). In the previously mentioned experiments (flow method), no substituted compound was found except C_2Cl_6 formed in the vapour phase. However, definite evidences of substitution were obtained when the static method was employed. Ethylene

(5) Effect of mercury lamp radiation may not be found so much noticeable unless more precise measurement is carried out.

(6) Unpublished data.

chloride was put in the vessel as shown in Fig. 2, the system was evacuated, and chlorine was passed in by opening the stopcock A, which was then closed. The temperature measured outside the vessel rose in one case from 16° to 21°, and in other cases, from 16.75° to 22.75° and from 17° to 47°.

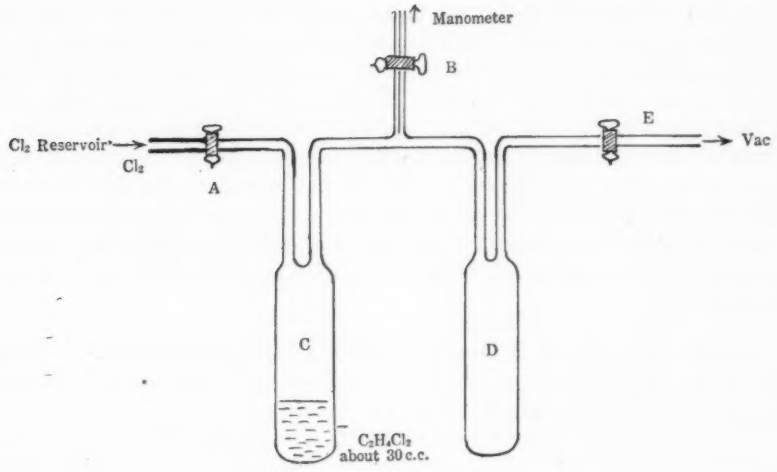

Fig. 2.

Moreover, the mercury-α-bromonaphthalene manometer indicated the rise of pressure from 14.35 cm. to 189.0 cm. at 17°, and from 76.0 cm. to 126.0 cm. at 18°.

At first the reaction is very slow, but after a certain time it becomes appreciable and gradually faster, showing a possible existence of an induction period. More experiments have been carried out and although they are not strictly quantitative, all of them have shown that chlorine, though slowly, reacts with ethylene chloride with the rise of temperature and increase of pressure. The increase of pressure is possibly due to the difference in solubilities of chlorine and hydrogen chloride in ethylene chloride. (Absorption of hydrogen chloride by ethylene chloride is now under investigation. The solubility of hydrogen chloride is much smaller than that of chlorine. The details will be published soon.) Hexachlorethane was noticed on the walls particularly at part D in Fig. 2 agreeing to the evidences found in the previous cases, and from the liquid part merely trichlorethane was obtained by fractional distillation. The formation of trichlorethane on mixing chlorine with ethylene chloride was demonstrated

again in the attempt[7] of measuring the solubility of chlorine in ethylene chloride; in this attempt no concordant results for the solubility were observed owing to the reaction between them.

Stewart and Smith[8] in the experiment of the reaction between ethylene and chlorine observed that, as soon as liquid ethylene chloride was formed on the wall of the reaction vessel, the rate of reaction became faster corresponding to the so-called induced substitution as caused by energy given out by excited ethylene chloride molecules, and they found trichlorethane and hydrogen chloride but no other higher chlorinated compounds. But the fact that ethylene chloride reacts with chlorine shows that trichlorethane formation is not necessarily be induced by addition reaction as suggested by Stewart and Smith. It can be independent, and furthermore, energy necessary for substitution can be supplied from other sources such as collision or possible excitation of chlorine to higher quantum states (Energy of excited chlorine as found from the spectral data is 0.233 volt[9] (heat of dissociation)).

Reaction Between Ethylene Chloride Vapour and Chlorine. In order to study the nature of the gaseous reaction between ethylene chloride and chlorine the following scheme has been carried out.

The reaction chamber was connected to the ethylene chloride reservoir and after allowing its vapour into the chamber, the stopcock was closed, the pressure of ethylene chloride vapour being maintained slightly lower than the saturated vapour pressure. The vapour was mixed with chlorine by opening the stopcock and after closing it the mixture was left for various lengths of time at various temperatures, the whole vessel being immersed in the thermostat. The experiments were carried out with mixtures in various proportions (Table 1).

Table 1.

Tem. (°C.)	$\frac{P_{Cl_2}}{P_{C_2H_4Cl_2}}$	Time (hrs.)
35	4.5	3
35	3	1/2
35	4	3
25	2.3	4
25	5	2½
25	2.3	3

The gaseous mixture was then condensed by cooling with liquid air or liquid nitrogen. It was found, however, that the reaction is extremely slow, and

(7) Discordant results have been found in several experiments of measuring the solubility of chlorine in ethylene chloride by a procedure somewhat similar to Taylor and Hildebrand's for measuring the solubility of chlorine in ethylene bromide, *J. Am. Chem. Soc.*, **45** (1923), 682.

(8) Stewart and Smith, *J. Am. Chem. Soc.*, **52** (1930), 2869; **51** (1929), 3091.

(9) International Critical Table, Vol. 5.

where chlorine is largely in excess hexachlorethane formation predominates in the gaseous phase and no other reaction is appreciable, while in the reaction between liquid ethylene chloride and chlorine there occurs trichlorethane formation especially on the surface (liquid-vapour interface) as semiquantitatively observed by the rise of temperature along the liquid-gas interface. This fact is concordant with the theoretical consideration that on the interface the concentration of chlorine is much higher than inside the body of ethylene chloride into which chlorine has been dissolved, favouring naturally the substitution reaction by chlorine.

Thus some important facts about the reactions between chlorine and ethylene chloride both in liquid and vapour phases have been pointed out, although they are not based strictly on quantitative data because of the complex nature of the reactions as well as lack of a suitable method of measurement. It is hoped that a more detailed study will be reported some time.

Some Suggestions for the Future Work. There are several investigators[10] who have studied infra-red absorption bands which are attributed to the carbon-hydrogen linkage in carbon hydrogen compounds as well as in their chlorine derivatives; furthermore Smith and Board[11] observed that substitution of chlorine for hydrogen in tetrachlorethane causes a remarkable decrease in the intensity of absorption in each of the characteristic absorption bands without any evident shift of its position, and a similar phenomenon takes place in the transformation from dichlorethylene to trichlorethylene. Such compounds as carbon disulphide and carbon tetrachloride have no such bands. Smith and Board[11] also state that the intensity is approximately a direct function of the number of hydrogen-carbon linkages. Later Spence and Easley[12] studied more carefully infra-red absorption bands of halogen derivatives of ethane, some fourteen compounds including the series of $C_2H_4Cl_2$, $C_2H_3Cl_3$, $C_2H_2Cl_4$, C_2HCl_5 and C_2Cl_6, and found that, as concluded by several previous investigators already, the mentioned absorption bands are due to carbon-hydrogen linkages, the intensity of absorption is a function of the number of C-H-linkages, and the bands completely vanish in hexachlorethane as in the case of carbon tetrachloride.

Looking over these papers, it is rather interesting to notice that the intensity of absorption decreases with chlorine substitution without shift of

(10) Ellis, *Phys. Rev.*, (2), **23** (1924), 48; *J. Opt. Soc. Am.* **8** (1924), 1; Coblentz, *Bur. Stand. Sci. Paper*, No. 148 (1921).

(11) Smith and Board, *J. Am. Chem. Soc.*, **48** (1926), 1512.

(12) B. J. Spence and M. A. Easley, *Phy. Rev.*, **34** (1929), 730.

the positions of bands, and that might be an available method for the study of chemical reactions in which chlorine substitution occurs and for which the ordinary conventional method of attack is not suitable, when the reaction is rather slow. Making use of the infra-red absorption phenomena we might be able to investigate chemical reactions which otherwise could not be easily studied. Whether it is practically useful or not must be decided by actual experiments.

Summary.

(1) In the reaction between chlorine and ethylene chloride in the liquid phase 1,1,2,-trichlorethane is the principal product and in the gaseous phase the formation of hexachlorethane predominates.

(2) The reaction between gaseous chlorine and liquid ethylene chloride seems to occur mainly on the liquid gas interface.

(3) Hydrogen chloride gas dissolved in the mixture catalytically accelerates the reaction.

(4) There seems to exist an induction period in the reaction between ethylene chloride and chlorine possibly owing to catalytic acceleration by either hydrogen chloride or substituted product or both in later stage.

(5) In the gaseous reaction between chlorine and ethylene chloride the formation of hexachlorethane predominates especially when chlorine exists largely in excess to ethylene chloride vapour.

(6) A suggestion is made as to the method of study on chemical reactions, especially on chlorination reaction (substitution).

In conclusion, the author wishes to express his hearty thanks to Prof. S. Mitsukuri for his interests and kind advices, and is also very grateful that a part of the expenses of this experiment were covered by the research funds granted to Prof. S. Mitsukuri by the Imperial Academy and the Saito Gratitude Foundation.

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CORRECTIONS

Volume 8, 1933.

Page	Line	
355	12	*for* "reveals a system of valency frequencies" *read* "has a system of fundamental frequencies"
„	13	*for* 1280 *read* (1285)

Volume 9, 1934.

Page	Line	
65	Title	*for* "DIPHENYL-2,2′-TERAZONIUM SULPHATE" *read* "DIPHENYL-2,2′-TETRAZONIUM SULPHATE"
58	21	*for* "(*oo*′-diphenylene)" *read* "(*oo*′-diphenylylene)"
68	17	*for* "H = 4.4%" *read* "H = 4.7%"
„	2*	*for* "(*oo*′-diphenylene)" *read* "(*oo*′-diphenylylene)"
131	9*	*for* "as chalcones" *read* "such as chalcones"
132	3	*for* "Piperonilideneacetophenone" *read* "Piperonylideneacetophenone"
„	4	*for* "Cinnamilideneacetophenone" *read* "Cinnamylideneacetophenone"
„	6	*for* "Dipipperonilideneacetone" *read* "Dipiperonylideneacetone"
133	1	*for* "Piperonilideneacetophenone" *read* "Piperonylideneacetophenone"
„	5	*for* "piperonilideneaceto-" *read* "piperonylideneaceto-"
133	16	*for* "potash" *read* "soda"
„	22	
168	18	*for* "$4H_22O$" *read* "$4H_2O$"
185	8	*for* "*m*-Nitrophénol" *read* "*p*-Nitrophénol"
234		*The top figure should be designated* "Fig. 19"
„	Legend to Fig. 20	*for* "nombres" *read* "numéros"
299	Fig. 26	*for* "A. $(NH_4)_3SO_4$" *read* "A. $(NH_4)_2SO_4$"
323	Fig. 1	*Two figures on the left being misplaced, their positions should be changed, and further add:* $\ominus\ Pt(CO)_n$ — $O\ Pt$ $\bullet\ [Pt(CO)Cl_3]$
359	1	*for* "cyclohexene" *read* "methylcyclohexane"
363	1	except Table *for* "menthene" *read* "menthane"
401	17	*for* "secend" *read* "second"
430	17	*for* "methylcyclohexylamine" *read* "cyclohexylamine"
485	6*	*for* "demmach" *read* "demnach"
„	5*	*for* "$\frac{d(\sigma\Omega)}{dT}$ constans" *read* "$\frac{d(\sigma\Omega)}{dT}$ = constans"
494	11	*for* "$CaO+K_2O/SiO_2$" *read* "$(CaO+K_2O)/SiO_2$"

* From bottom.